



## Catalytic wet air oxidation of olive oil mill effluents

## 4. Treatment and detoxification of real effluents

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## ABSTRACT

Olive oil mill wastewater (OMW) generated by the olive oil extraction industry constitutes a major pollutant, posing severe environmental threats. It contains a high organic load and phytotoxic and antibacterial phenolic compounds which resist biological degradation. Platinum and ruthenium supported titania or zirconia were studied in the catalytic wet air oxidation (CWAO) of OMWs in a batch reactor and in a continuous trickle-bed reactor. CWAO experiments at 190 °C and 70 bar total air pressure confirmed the effective elimination of the TOC (total organic carbon) and of the phenolic content of actual diluted OMW. Simultaneously, toxicity towards *Vibrio fischeri* was reduced and a decrease in phytotoxicity occurred. The ruthenium catalysts were found stable over a long period of operation in a trickle-bed reactor.

The biodegradability of the oxidized waste has been enhanced and this study also examined the feasibility of coupling CWAO and an anaerobic digestion treatment. The pretreatment of the OMW in the presence of a ruthenium catalyst reduced considerably the total phenolic contents of the wastewater, and produced an effluent suitable to be treated by anaerobic treatment with increased biomethane production compared to the untreated effluent.

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## 1. Introduction

Usually, olive oil is extracted mechanically by conventional pressing or by continuous centrifugation methods. This extraction process results in the production of olive oil mill wastewater (OMW); the first process leads to about 50% of OMW by weight of milled olives, while the latter process generates 80–110% of OMW due to the continuous washing of the olive paste [1]. For the Mediterranean countries, the production of this liquid effluent is estimated at 7–30 millions m<sup>3</sup> year<sup>-1</sup>. The disposal and the treatment of this liquid waste constitute a critical environmental problem, because of the high organic load (chemical oxygen demand, COD as high as 200 g/L) and the high content of polyphenols responsible for the phytotoxic and antibacterial effect (up to several grams per liter). As a result of the presence of these compounds, OMW resists biological degradation [2].

The most common elimination method is through evaporation in storage ponds [3] or through controlled use for fertirrigation in

few countries. In recent years, severe limitations were introduced, and these methods, which can only marginally meet the stringent environmental regulations, are no longer satisfactory. Therefore, several treatment options have been proposed before the release of OMW into the environment [4,5]. Physicochemical treatment such as adsorption, lime precipitation [6], electrocoagulation [7], electrooxidation [8], flocculation and coagulation [9,10], ultra-filtration/reverse osmosis [11],... have been proposed. There is also an interest in biological treatments such as anaerobic digestion for biogas production and potential re-use of the effluent in irrigation [12,13]. The major limitation of the performance of anaerobic digestion is the presence of phenols, given their biorecalcitrant and/or inhibiting character [14,15]. Consequently, a pretreatment stage is necessary to remove these undesirable compounds.

Chemical oxidations using clean oxidants (oxygen, hydrogen peroxide, and ozone) are also promising treatment technologies that reduce significantly COD and BOD and that have received increasing interest. An overview of the so-called Advanced Oxidation Processes (AOP) for treatment of OMW is given in [5]. These AOP processes rely on the generation of free hydroxyl radicals OH<sup>•</sup> and include ozone, UV radiation, hydrogen peroxide, Fenton reagent, photocatalysis, ... or various combinations. Among

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the oxidation technologies, wet air oxidation is also increasingly used for the elimination of a variety of organic contaminants in wastewaters from different industries. Supercritical wet air oxidation (500 °C, 250 bar) was used to degrade a ~50 times diluted OMW (initial COD = 3.3 g/L) with 99.9% COD removal and 98% phenol removal after 1–3 min [16]. Under subcritical conditions, an OMW diluted ~10 times with a municipal wastewater (TOC = 4.9 g L<sup>-1</sup>) treated with 2 g L<sup>-1</sup> CuO/C or Pt/Al<sub>2</sub>O<sub>3</sub> catalysts with or without H<sub>2</sub>O<sub>2</sub> at 180 °C and 70 bar pressure, gave ~50% COD removal and 80% phenol removal after 6 h [17]. Also, Pt/C and Ir/C catalysts showed a high efficiency in the wet air oxidation of an OMW from a continuous three-phase centrifugation process (COD<sub>i</sub> = 60.5 g L<sup>-1</sup>) after dilution to COD = 2.8 g L<sup>-1</sup> at 200 °C and 6.9 bar of oxygen partial pressure [18]. In a previous work, we have reported on the results obtained in the catalytic wet air oxidation of representative phenolic pollutants of OMW over platinum and ruthenium supported TiO<sub>2</sub> and ZrO<sub>2</sub> in a stirred batch autoclave and in a fixed bed reactor [19–21]. From these studies, it was concluded that the CWAQ could be successfully used in the removal of phenolics like *p*-coumaric acid, *p*-hydroxyphenylacetic acid or *p*-hydroxybenzoic acid at 140 °C and 50 bar total air pressure. Ruthenium supported catalysts were found stable under these conditions.

The aim of this work was to investigate the performances of the Pt and Ru catalysts developed previously for the CWAQ treatment of real OMW to reduce the organic load. The aim was also to examine the efficiency of CWAQ as a possible method for effective pretreatment to reduce the concentration of toxic and inhibitory compounds in OMW such as the phenolic compounds to improve the biodegradability. Thus, we performed a comparative study in terms of methane yield of the anaerobic digestion of untreated and previously treated OMW. CWAQ experiments were performed on different OMWs in batch and continuous reactors at 190 °C and 70 bar air operating pressure.

## 2. Materials and experimental methods

### 2.1. Olive oil mill wastewaters

The crude OMW used in this study was obtained from:

- A super-press olive oil production plant in Tunisia (Cooperative oléicole, Sfax). Crude OMW was also separated into different fractions by ultrafiltration (Gamma Filtration, France) through multi-tubular polysulfonate organic membranes (PCI) with different cut-off at 8, 25 and 100 kDa [14]. The molecular-mass fractions chosen were the low molecular-mass fraction (KD8, <8 kDa) and the high molecular-mass fraction (KD100 > 100 kDa).

- An olive oil mill from a plant in southern Italy which uses the classical three-phase continuous centrifugation system.

Fresh OMW was transported to our laboratory under refrigeration within 1 h of its production and in order to conduct the tests with the same wastewater, appropriate amounts of OMW were distributed in 1 L plastic bottles and stored at -20 °C until use. At the time of the use, the OMW sample was thawed in a refrigerator and centrifuged 6000 trs/min for 20 min to remove suspended solids. In some experiments OMW was diluted by a factor ranging from 1 to 70. The diluted OMWs will be named *x*%OMW, with *x* the dilution factor.

### 2.2. Catalyst preparation and characterization

Catalysts were prepared using powder or pelleted commercial titanium oxide and zirconium oxide. Deposition of ruthenium or platinum (3 wt.%) was carried out by incipient-wetness impregnation with an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub>, RuCl<sub>3</sub> or Ru(NO)(NO<sub>3</sub>)<sub>3</sub>, as described elsewhere [19–21]. After drying, the catalyst precursors were reduced in flowing H<sub>2</sub> at 300 °C and passivated in a 1%O<sub>2</sub>/N<sub>2</sub> flow.

Table 1 summarizes the textural properties of the catalysts studied in this study. More detailed characterizations were published elsewhere [19–21].

### 2.3. Catalytic wet air oxidation experiments

The batch experiments were performed in an autoclave of 280 mL equipped with a magnetically driven stirrer and a valve for sampling [19]. Typically, 150 mL of the wastewater was treated. After flushing with argon, the reactor was heated to the desired temperature. Pressurization with air was then completed and time zero of reaction was considered. The continuous experiments were performed in a laboratory-scale high-pressure fixed-bed reactor with co-current down-flow of liquid and gas phases. The system consisted of a tube made of Hastelloy C (1 cm i.d. and 15 cm height). The details of experimental set-up and experiment description can be found elsewhere [21].

During the reactions, samples were taken at regular intervals to measure the TOC and the total phenol contents. The TOC was determined with a Shimadzu 5050 TOC-analyzer, whose operation is based on the combustion/non dispersive infrared gas analysis method (NDIR). The total phenol content was determined colorimetrically using the Folin–Ciocalteu reagent (ability of phenolic compounds to reduce the phosphomolybdic–phosphotungstic reagent) [22]. A diluted sample or phenolic standard was mixed with the Folin–Ciocalteu reagent and 1 mL of a sodium carbonate saturated solution. The final solution was left in the dark for 1 h, after which the absorbance of the solution

**Table 1**  
Catalysts used in this study

Support	Supplier	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Average pore diameter (nm)	Catalyst
TiO <sub>2</sub> P25	Degussa	50	Non-porous	3%Pt/TiO <sub>2</sub> P25
TiO <sub>2</sub> DT51	Millenium	90	9	3%Pt/TiO <sub>2</sub> DT51 3%Ru/TiO <sub>2</sub> DT51 ex NO 3%Ru/TiO <sub>2</sub> DT51 ex Cl
ZrO <sub>2</sub> Mecat XZO/023	Melcat	92	9	3%Ru/ZrO <sub>2</sub> Mel ex NO 3%Ru/ZrO <sub>2</sub> Mel ex Cl
TiO <sub>2</sub> G	St Gobain	36	21.5	3%Ru/TiO <sub>2</sub> G
ZrO <sub>2</sub> G	St Gobain	104	10.7	3%Ru/ZrO <sub>2</sub> G

was measured at 750 nm and compared against a blank prepared following the same protocol but without any sample. Method was calibrated with gallic acid solutions of known concentration. Total phenol values were expressed as gallic acid equivalents (mg/L).

Phenolic compounds in OMW samples were analyzed by HPLC on a C18 column. The mobile phase used was 0.1% phosphoric acid in water (A) versus 70% acetonitrile in water (B) for a total running time of 50 min, and the following proportions of solvent B were used for the elution: 0–30 min, 20–50%; 30–35 min, 50%; and 35–50 min, 50–20%. The flow rate was 0.6 mL min<sup>-1</sup>, and the injection volume was 20 µL [23].

Size exclusion HPLC was performed in order to determine the distribution of phenolic compounds using a Progel TSK-G 2000SW Supelco column. The elution was carried out using a phosphate buffer pH 6.8 and 0.6 mL min<sup>-1</sup> flow rate. The wavelength of the detector was adjusted to 280 nm.

#### 2.4. Micro and phytotoxicity

A LUMISTox 300 luminometer, a LUMISterm incubator, and the non-pathogenic bacteria *Vibrio fischeri* LCK 480 (liquid dried), all obtained from Dr. Lange GmbH, Düsseldorf, Germany, were used for acute toxicity measurements. The test consisted in the inhibition of the bioluminescence of *V. fischeri* according to ISO 11348-2 [24]. Since the luminescent bacterium requires marine conditions, solid sodium chloride crystals were added to the OMW and soil extract samples to obtain a final concentration of 2% (w/v). The pH was adjusted to 7.0 ± 0.2. Dilutions of OMW and soil extracts were carried out with 2% sodium chloride solution according to Dr. Lange LUMISTox operating manual. Percentage inhibition of the bioluminescence was achieved by mixing 0.5 ml of OMW or soil extract and 0.5 ml luminescent bacterial suspension. After a 15 min exposure at 15 °C, the decrease in light emission was measured. The toxicity of the OMW and soil extract was expressed as the percent of the inhibition of bioluminescence (%I<sub>B</sub>) relative to a non-contaminated reference. Blank (Milli-Q water containing 2% NaCl) and positive control (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 4.0 mg L<sup>-1</sup> and NaCl 7.5%) solutions were used with each batch of bacteria to verify bacteria and reagent quality.

The phytotoxicity of the resulting effluent was estimated using *Lycopersicon esculentum* (tomato) seeds according to [25].

10 tomato seeds were placed on papers in standard Petri dishes. OMW samples were added to the seeds and paper and the dishes were placed in an incubator at 25 °C for 72 h. Blank samples were also run with water. Phytotoxicity was measured for samples at different dilutions. The germination index was calculated and expressed as the percentage of germinated seeds.

#### 2.5. Biodegradation tests

The fermentations were carried out in 1000 mL glass bottles containing 500 mL working volume as already described [26]. They were filled with the sample (OMW or pretreated OMW) at same desired concentration (1 g COD L<sup>-1</sup>). Inoculum was provided by an OMW treating anaerobic filter reactor. A total of 5 g COD of OMW (pretreated or not pretreated) were filled discontinuously per anaerobic batch as soon as the biogas production is almost null. The anaerobic conditions in filling operation were maintained by continuously flushing with nitrogen gas. The bottles were then incubated at the temperature of 37 °C and magnetically stirred. The volume of biogas produced was measured by a displacement method. Gas samples were taken with a syringe from gaseous phase and the methane was determined by gas-chromatography with a TCD detector.

### 3. Results and discussion

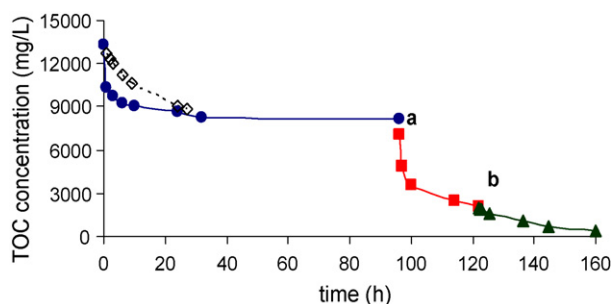
#### 3.1. Characterization of the real OMWs

Table 2 shows the characteristics of the filtered OMWs used in this work.

All OMWs were very dark colored and foul-smelling. They were characterized by an acidic pH (4.7–5.4) and a high concentration of TOC (in the range 14–70 g L<sup>-1</sup>). The Tunisian effluents MTB, and the fractions KD8 and KD100 contain a much higher concentration of inorganic ions than the Italian effluent MIB, which may be due to the different olive oil extraction procedures or to the nature of the soils, the fertilizers or the quality of water. Indeed, groundwater and tap water in the south of Tunisia may contain high concentrations of chloride. The inorganic cations are mainly K, Na, Ca and Mg. Very low amounts of phosphorus or sulfur are measured. The high value of 13.4 of the COD/BOD<sub>5</sub> of fraction KD100 containing complex polyphenolics shows that it is hardly

**Table 2**  
Analysis of initial OMWs

	MIB	MTB	KD8	KD100
Color	Yellow-grey	Black	Dark brown	Black
pH	4.7	5.4	5.4	5.4
TOC (g L <sup>-1</sup> )	ca. 17	47.5	14	70
Total phenols (g L <sup>-1</sup> )	3.2	29	nm	24
COD	nm	nm	65.5	187.5
COD/BOD <sub>5</sub>	nm	nm	4.9	13.4
EC <sub>50</sub>	nm	nm	<0.005%	>0.7%
Species in solution (mg L <sup>-1</sup> )				
Cl <sub>total</sub> (Cl <sup>-</sup> )	680 (620)	6200 (2380)	1800 (1630)	2700 (2070)
P <sub>total</sub> (PO <sub>4</sub> <sup>3-</sup> )	255 (720)	470 (1530)	170 (350)	400 (520)
S <sub>total</sub> (SO <sub>4</sub> <sup>2-</sup> )	850 (180)	314 (710)	300 (920)	581 (970)
N <sub>total</sub> (NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup> )	<0.1% (<2, 2.2)	0.23% (<2, 39)	<0.1 (<2, 39)	0.23% (6,9)
Na	95	290	450	780
Ca	138	690	530	190
Mg	140	300	190	450
K	4000	8800	3500	7000
Al	2	4	4	80
Si	10	nm	<12	220
Fe	10	30	2	85
Ni	<1	<2	<2	<2



**Fig. 1.** TOC concentration profile during the oxidation of crude KD8 in the presence of 3%Ru/ZrO<sub>2</sub> MeI ex NO. Reaction conditions: 150 mL OMW, ( $\diamond$ )  $T = 140^\circ\text{C}$ , ( $\bullet$ ,  $\blacksquare$ ,  $\blacktriangle$ )  $T = 190^\circ\text{C}$ , 70 total air pressure, 1 g catalyst. (a) After cooling, catalyst was separated and 100 mL of the liquid residue was submitted to a new run with addition of fresh catalyst, (b) after cooling, gaseous atmosphere was renewed.

biodegradable, while fraction KD8 containing monophenols, o-diphenols, monomeric flavonoids, hydrolysable tannins and anthocyanins with a COD/BOD<sub>5</sub> ratio of 4.9 could be more easily treated biologically [14]. The comparison of the *V. fischeri* test shows that fraction KD8 is more toxic than fraction KD100. The MIB wastewater also contains large amounts of suspended solids.

### 3.2. CWAO treatment of real OMW in batch experiments

#### 3.2.1. Preliminary evaluation of CWAO treatment of crude OMWs

A series of preliminary experiments was carried out in the stirred batch reactor with the crude OMWs by treating 150 mL of aqueous wastes at 140 or 190 °C and 70 bar of air total pressure. It should be pointed out that considering the very high TOC content of the raw OMWs (14–70 g L<sup>-1</sup>), the availability of oxygen should not be sufficient for a total mineralization of TOC under these conditions, and the maximum mineralizable TOC would be around 4 g L<sup>-1</sup>.

Fig. 1 shows the evolution of TOC concentration during the catalytic treatment of effluent KD8.

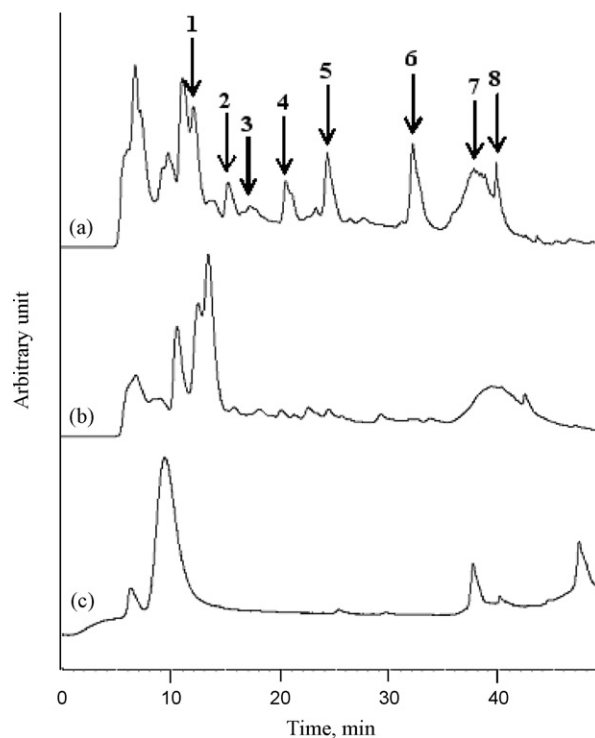
In the absence of a catalyst, the treatment of the crude OMWs produced large amounts of black solid matter, probably due to the polymerization of phenolic compounds. The treatment of OMW in the presence of 3%Ru/ZrO<sub>2</sub> MeI ex NO catalyst reduced considerably the TOC concentration. At 190 °C and after 6 h of reaction, it was reduced from 13.4 to 9.2 g L<sup>-1</sup>. A conversion plateau was then observed at ca. 4.14 g L<sup>-1</sup> TOC mineralized, a value close to that expected from the limited availability of O<sub>2</sub>. Simultaneously the dark brown color became slightly lighter. At 140 °C, the mineralization was slower and this limit was attained after 27 h of treatment.

After the reaction at 190 °C, the effluent was recovered and 100 mL was subjected to a new experiment with a fresh catalyst (Fig. 1a). The TOC concentration still decreased to 2.1 g L<sup>-1</sup> and the brown color of the OMW became brighter and colorless as the reaction proceeded. Finally, in a third step, after cooling, the gaseous atmosphere was renewed (Fig. 1b). Near total mineralization of effluent KD8 was obtained (TOC = 0.39 g L<sup>-1</sup>), while the effluent became light yellow. The elemental analysis of the final effluent revealed no leaching of Ru or Zr at the detection limit.

Fig. 2 shows the HPLC chromatograms of KD8, before and after reaction at 140 and 190 °C. Reaction at 140 °C was capable of substantially reducing the concentration of the majority of identified compounds present in the untreated sample, while they have nearly disappeared after treatment at 190 °C.

The biotoxicity determined by the *V. fischeri* test at different dilutions of the effluents is given in Fig. 3 for KD8.

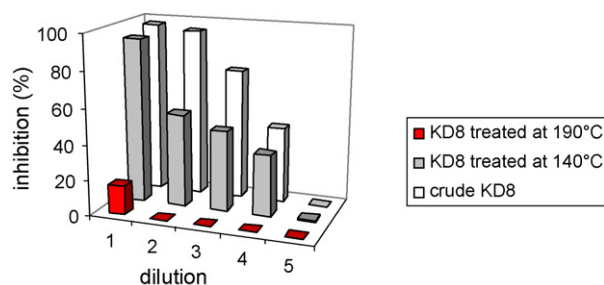
Untreated KD8 exercised nearly 100% inhibition of luminescence after dilution factor of 1 or 2; further dilution decreased the



**Fig. 2.** Distribution by HPLC of monophenolic compounds present (a) in KD8 fraction, (b) after reaction at 140 °C, and (c) after successive oxidations at 190 °C in the presence of 3%Ru/ZrO<sub>2</sub> MeI ex NO catalyst. Identified peaks: 1 = hydroxytyrosol, 2 = 3,4-dihydroxyphenylacetic acid, 3 = tyrosol, 4 = 4-hydroxyphenylacetic acid, 5 = caffeic acid, 6 = vanillin, 7 = ferulic acid, 8 = oleuropein (ester of elinolic acid and hydroxytyrosol).

inhibition effect. After treatment at 140 °C, the toxicity was reduced but it was still at 52% inhibition at the dilution of 2, due to the presence of high organic load, of which phenolic compounds (Fig. 2). After catalytic treatment at 190 °C and a nearly complete conversion of TOC (>97%), the effluent exhibited only 17% inhibition and a dilution of 2 permitted the elimination of the luminescence inhibition.

Finally, the effectiveness of KD8 detoxification was assessed by germination tests, using *L. esculentum* seeds. It is generally accepted that OMW phytotoxicity is largely due to the presence of phenolic compounds, although other OMW constituents such as carboxylic acids are also known to be phytotoxic [27]. As expected, crude KD8 was strongly phytotoxic with a germination index of 8%. However, even though >97% TOC was removed after treatment at 190 °C, only a partial reduction of phytotoxicity was observed with an increase of germination index to 38% after treatment at 190 °C. The high salinity of the OMW could be partially responsible for the incomplete removal of phytotoxicity.



**Fig. 3.** Relative toxicity of crude KD8 and effluents collected after CWAO treatment at 140 and 190 °C in the presence of 3%Ru/ZrO<sub>2</sub> MeI ex NO.



### 3.2.2. Treatment of diluted OMWs

The results of the screening experiments clearly showed that, at the conditions used, the wet air oxidation process in the presence of a ruthenium catalyst can partially decontaminate the crude OMW. Because it was not possible with the present reactor to operate under oxygen excess conditions, wastewater had to be diluted prior to its oxidation. Therefore, in the subsequent experiments, the OMW samples were diluted 3.75–70 times with deionized water (referred to as  $x\%$ OMW). OMW samples with nearly the same initial organic load were treated in the absence of a catalyst or in the presence of the platinum and ruthenium catalysts previously tested in model compounds [19–21].

Fig. 4 shows the TOC concentration-time profiles obtained in the oxidation of 3.75%KD8, 15%KD100 and 10%MTB, diluted to initial TOC concentrations around 4–5 g L<sup>-1</sup> in the presence of selected platinum and ruthenium catalysts.

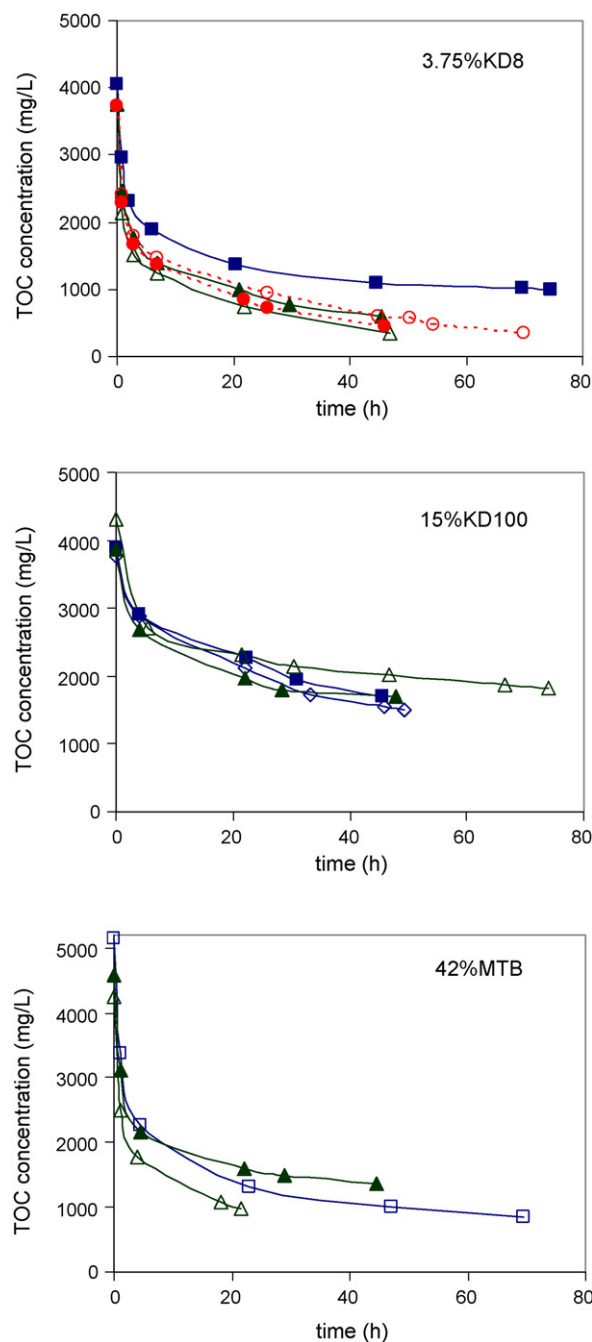
In all experiments performed in the absence of catalysts, the TOC concentration could not be measured accurately in the samples withdrawn from the autoclave, because of the formation of polymeric products sticking to the reactor wall, as detected at the opening of the reactor. In the presence of catalysts, no polymers were observed and the TOC concentration profiles as a function of reaction time were similar in the wet air oxidation of the different diluted OMWs in the presence of the different catalysts. Interestingly, degradation increased significantly in the presence of the catalyst. Most of the mineralization was achieved in the first hours of the reaction. With additional time, TOC smoothly decreased. At long reaction times, the curves showed a saturation profile, due to the presence of refractory molecules (such as carboxylic acids). From these experiments, it was not clear if the nature of the metal, the precursor salt or the support of the catalyst had an influence on the performances of the catalyst, since the extent of degradation was nearly the same for a given wastewater. It was also noticed that under the same operating conditions, the conversion reached a plateau in the treatment of 15%KD100 at a higher concentration of TOC than in the treatment of 3.75% KD8 and 10% MTB. This suggests that molecules present in that effluent such as high molecular-mass polyphenols are less easily degraded.

The effluents at the final stage of treatment did not contain any detectable elements leached from the catalyst (Pt < 0.3 ppm, Ru < 0.5 ppm).

The toxicity of these effluents has been imputed to phenolic compounds, because they are phytotoxic and they inhibit the anaerobic biological treatment. The total phenol content measured for the experiment performed with 3.75%KD8 in the presence of 3%Pt/TiO<sub>2</sub> p25 showed the beneficial effect of the addition of the catalyst. Indeed, the phenol content (initially at 722 mg L<sup>-1</sup>) decreased markedly, and only traces were detected in the final effluent. Additionally, the treated 15%KD100 effluent was characterized by size exclusion chromatography (SE-HPLC) for the molecular mass distribution of phenolic compounds. 15%KD100 exhibits a large peak corresponding to complex polyphenols. Following treatment at 190 °C in the presence of 3%Pt/TiO<sub>2</sub> p25, the overall area of absorbance peaks was reduced and the MW distribution was shifted towards lower MW values (higher retention times).

Effluent toxicity for *V. fischeri* was also measured before and after treatment of 3.75%KD8 and 15%KD100. The results are shown in Fig. 5.

The untreated solutions 3.75%KD8 and 15%KD100 were highly toxic as shown by the 74% and 90% inhibition at dilution 1, respectively. As expected, this inhibition was reduced as the dilution factor increased. After treatment, the percentage of inhibition was decreased to 43–46% whatever the catalyst, which means that roughly half of the toxicity was eliminated. However,



**Fig. 4.** Evolution of TOC as a function of time during oxidation of 3.75%KD8, 15%KD100 and 10%MTB in the presence of platinum and ruthenium catalysts. Reaction conditions: 150 mL effluent, 190 °C, 70 bar operating air pressure, 0.5 g catalyst. (■) 3%Pt/TiO<sub>2</sub> p25, (□) 3%Pt/TiO<sub>2</sub> DT51, (▲) 3%Ru/TiO<sub>2</sub> DT51 ex NO, (△) 3%Ru/TiO<sub>2</sub> DT51 ex Cl, (○) 3%Ru/ZrO<sub>2</sub> Mel ex Cl.

although high mineralization degrees were achieved and concentration of phenolic compounds was reduced, the residual toxicity remained high. This biotoxicity after oxidation may be related to some of the oxidation products. It was also noticed that this inhibition remained at a higher value when ruthenium catalysts were used compared to platinum catalysts. This effect might be attributed to the presence of short chain carboxylic acids, which are more prone to be formed on ruthenium catalyst.

In a final series of experiments, OMWs diluted to TOC<sub>0</sub> = ca. 1 g L<sup>-1</sup> were investigated with a catalyst loading of 0.5 g, at 190 °C and 70 bar total air pressure, with the objective to better select the

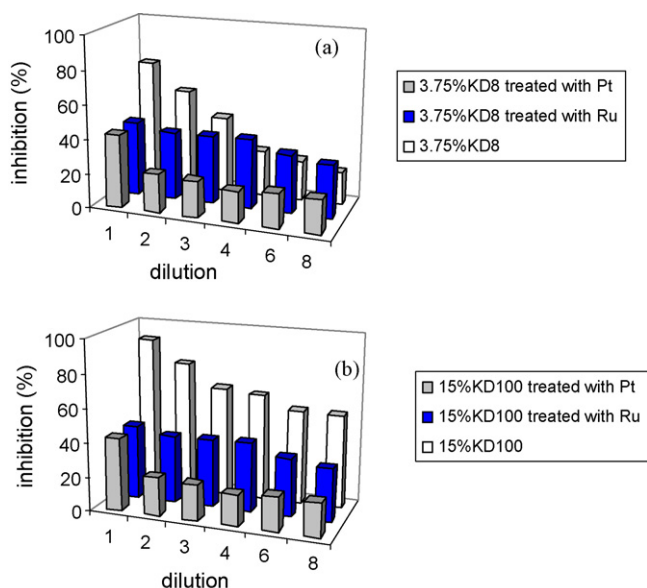


Fig. 5. Biotoxicity measured by the *Vibrio fischeri* test of (a) 3.75%KD8 and (b) 15%KD100, untreated and after treatment with 3% Pt/TiO<sub>2</sub> P25 or 3% Ru/TiO<sub>2</sub> DT51 exCl.

optimum catalyst. Fig. 6 illustrates the TOC profiles during the treatment of 70%KD100, 42%MTB and 15%MIB.

In the absence of a catalyst, the samples of these diluted effluents withdrawn from the reactor contained suspended matter in the first few hours, but were then homogeneous. The TOC analysis indicated a maximum of 50% extent of degradation for the three diluted effluents. However, when the same runs were performed in the presence of the supported catalysts, TOC conversion increased greatly. The organic load decreased continuously with time with fast removal rate of TOC in the first hours of the reaction. Ruthenium catalysts were generally more active than platinum catalysts in terms of final TOC reduction. For instance, with 3%Ru/ZrO<sub>2</sub> Mel ex NO catalyst, a 96% TOC abatement was achieved after 24 h in the treatment of 15% MIB effluent, while the conversion attained only 76% after 22 h in the presence of 3%Pt/TiO<sub>2</sub> P25. Similarly, in the oxidation of 70%KD100, the extent of TOC abatement was lower in presence of 3%Pt/TiO<sub>2</sub> P25 (77% after 4 h) than in the presence of 3%Ru/TiO<sub>2</sub> DT51 ex NO or 3%Ru/ZrO<sub>2</sub> Mel ex NO (87% and 90%, respectively). According to the literature and our results [28,29], the difference can be explained in terms of generation of intermediates, mainly carboxylic acids, that are not further oxidized with platinum catalysts and consequently accumulate in the system. Furthermore, analysis of the total phenol in all treated effluents revealed that the phenolic compounds have totally disappeared. Again, no Ru, Ti or Zr could be measured within ICP-AES detection limit (Pt < 0.2 ppm, Ru < 0.5 ppm, Ti < 0.1 ppm, Zr < 0.5 ppm). Effluent toxicity was also measured before and after treatment. The effluent 42% MTB exhibited an inhibition of 81% of the luminescence. After reaction in the presence of 3% Ru/TiO<sub>2</sub> DT51 ex NO or 3%Pt/TiO<sub>2</sub> DT51 ex NO, although nearly complete mineralization was observed, the treated effluent had still a negative effect, as already shown in Fig. 3. The inhibition was only slightly reduced to 67% and 73%, respectively (dilution factor 1).

To verify the role of the different catalysts, additional experiments were carried out. The reaction was started with a platinum catalyst up to 56–60% TOC abatement. Then, after cooling, a fresh platinum or ruthenium catalyst was added and the reaction pursued. The results are shown in Fig. 7.

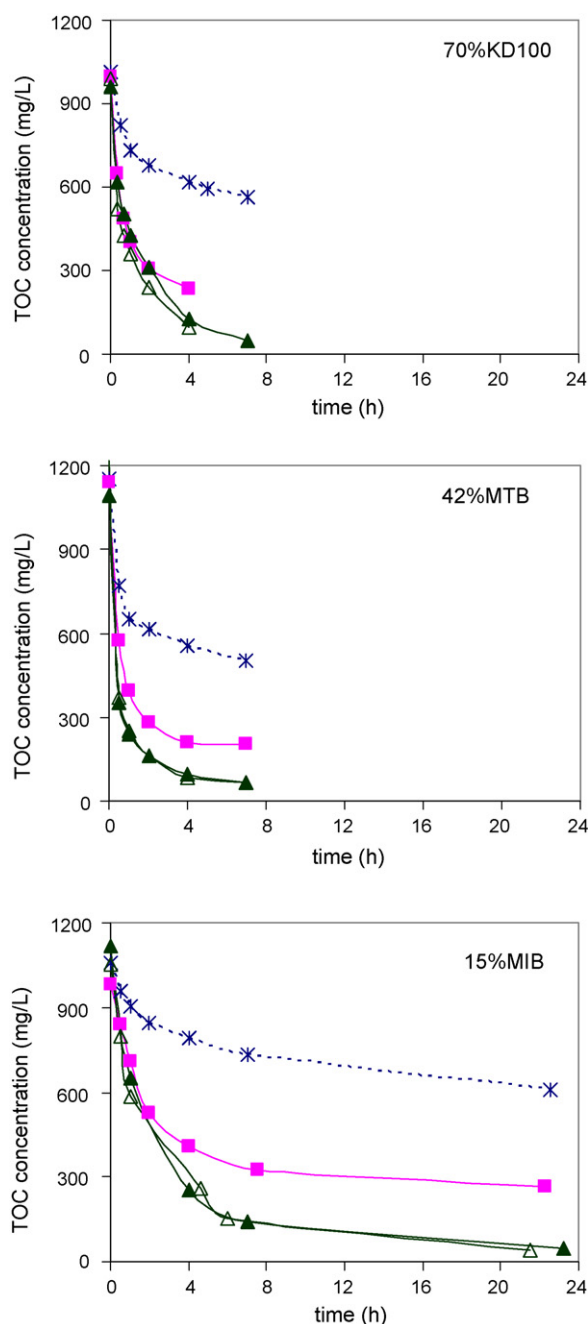
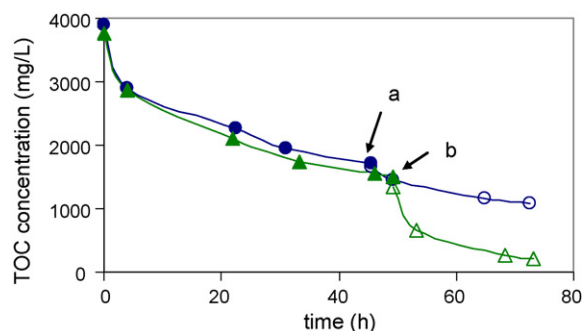


Fig. 6. Evolution of TOC as a function of time during oxidation of 70%KD100, 42%MTB and 10%MIB in the presence of platinum and ruthenium catalysts. Reaction conditions: 150 mL effluent, 190 °C, 70 bar air operating pressure, 0.5 g catalyst. (\*) No catalyst, (■) 3%Pt/TiO<sub>2</sub> P25, (▲) 3%Ru/TiO<sub>2</sub> DT51 ex NO, (△) 3%Ru/ZrO<sub>2</sub> Mel ex NO.

The introduction of a fresh platinum catalyst did not affect the efficiency of the treatment, and TOC concentration decreased only slightly upon further treatment. On the contrary, nearly complete mineralization of the liquid residue was obtained by introduction of the ruthenium catalyst, which could be explained by the ability of the ruthenium catalyst to degrade the carboxylic acids formed in the first stage.

### 3.3. CWAO of real OMW in the trickle-bed reactor

The stability of the catalyst in the implementation of this technique is a necessary step, which was investigated in a trickle-

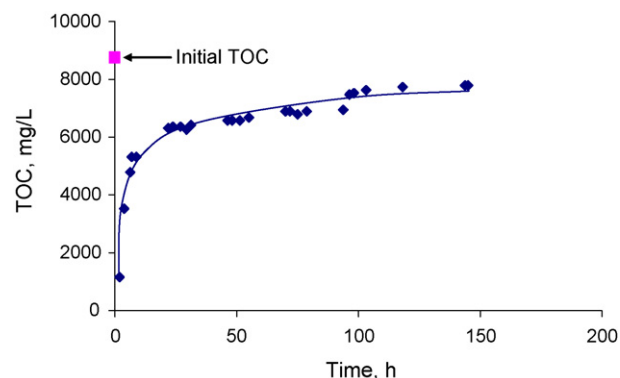


**Fig. 7.** TOC concentration during successive oxidation of 15%KD100 in the presence of 3%Pt/TiO<sub>2</sub> p<sub>25</sub> and addition of fresh (a) 3%Pt/TiO<sub>2</sub> p<sub>25</sub> or (b) 3%Ru/ZrO<sub>2</sub> Mel exCl<sup>-</sup>.

bed reactor operating with co-current down-flow mode of liquid and gases. The catalysts used in this study were 3%Ru/ZrO<sub>2</sub> G or 3%Ru/TiO<sub>2</sub> G (grains 0.3–0.7 mm), prepared by wetness impregnation with aqueous solutions of ruthenium nitrosyltrinitrate. Two sets of experiments were performed with diluted MTB and MIB. These continuous experiments were conducted as was described previously in the continuous oxidation of aqueous solutions of model pollutant 4-hydroxybenzoic acid [21].

Effluent MTB was centrifuged to separate the pulps and to get a homogenous liquid fraction. The initial TOC of this raw effluent (47.5 g/L) was lowered to 930 mg/L by dilution with permuted water. The feed  $F_L$  consisted of 24 mL/h of this effluent ( $F_L = 0.022 \text{ g}_{\text{TOC}} \text{ h}^{-1}$ ) which was flown through the 3%Ru/ZrO<sub>2</sub> G catalyst bed (1.5 g,  $W_{\text{Ru}} = 0.045 \text{ g}$ ) held at 190 °C and 50 bar air at 5 L/h. This corresponded to a space time of  $W_{\text{Ru}}/F_L$  of 2 h  $\text{g}_{\text{Ru}} \text{ g}_{\text{TOC}}^{-1}$ . Under these conditions, the oxygen was largely in excess for the total mineralization of the effluent to CO<sub>2</sub>. The reactor was heated with a flow of water, and when the temperature reached 190 °C, the water was replaced with the effluent. After a few days, the solution collected during the continuous steady-state operation was recovered, and re-used over the catalyst bed. This operation was repeated a second time. The evolution of TOC concentration as a function of time on stream is shown in Fig. 8. There were some process upsets that occurred in the first stage of the operation, which had little effect on the activity of the catalyst when the experiment was restored.

At the start of the reaction, when water flown through the catalyst was replaced by the OMW (TOC = 931 mg L<sup>-1</sup>) at a space time of 2 h  $\text{g}_{\text{Ru}} \text{ g}_{\text{TOC}}^{-1}$ , the TOC value increased significantly during ca. 20 h. This is the time required for the displacement of water by the effluent [21]. Then, it still increased progressively up to about 80 h. This second period corresponds to the time required to achieve a stable oxygen coverage of the ruthenium surface, as



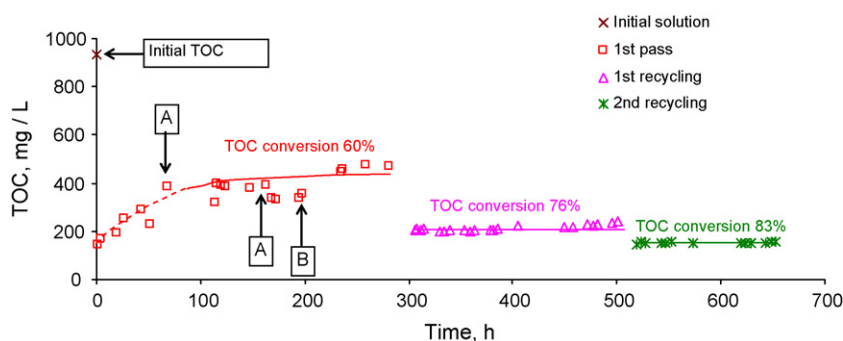
**Fig. 9.** TOC concentration as function of time on stream in the oxidation of 2%MIB in the presence of 3%Ru/TiO<sub>2</sub> G at 190 °C, 50 bar air, space time 0.43  $\text{g}_{\text{Ru}} \text{ h g}_{\text{COT}}^{-1}$ .

already observed during oxidation of *p*-hydroxybenzoic acid, under similar reaction conditions [21]. The catalyst was then quite stable, running at high TOC conversion over this period. A conversion of 60% was achieved.

During the re-use of the solution, the catalyst remained still very stable. TOC conversion of 76% and 83%, respectively, could be achieved during the 1st and the 2nd re-use with increasing space time. The effluent was rapidly discolored. Besides, the phenolic content of the wastewater, initially at 580 mg L<sup>-1</sup>, was significantly reduced during the process (50 mg L<sup>-1</sup> after the 1st pass, 3 mg L<sup>-1</sup> after the 1st re-use) with a nearly complete removal in the final effluent (0.8 mg L<sup>-1</sup>). The analysis of this final treated effluent did not show any trace of ruthenium by ICP-AES (within the detection limits of 0.5 ppm). The initial diluted MTB was highly colored. The color intensity of the effluent decreased considerably as a result of phenolic compounds removal.

The beneficial effect of CWAO was also demonstrated in a new set of experiment conducted with a more concentrated effluent. The as-received MIB effluent was centrifuged (5000 rpm, 30 min), filtered to eliminate the solid matters, and diluted twice with deionized water to an initial TOC of 8730 mg L<sup>-1</sup>. The reaction conditions were the same as described previously, using 3 g of 3%Ru/TiO<sub>2</sub> G catalyst and the reaction was carried out as described above. The initial space time was 0.43 h  $\text{g}_{\text{Ru}} \text{ h g}_{\text{COT}}^{-1}$  and by re-use of the solution it was progressively increased to 3  $\text{g}_{\text{Ru}} \text{ h g}_{\text{COT}}^{-1}$  over a total period of operation of 500 h. The results are shown in Fig. 9 for the initial part of the reaction.

After an initial deactivation due to stabilization of the oxidation state of the catalyst, the TOC value was almost constant (average TOC conversion of 19% for this pass). After 145 h of reaction, 3.5 L of the treated effluent was recovered. One third of this solution was



**Fig. 8.** TOC concentration as a function of time on stream during the continuous wet air oxidation of diluted MTB in the presence of 3%Ru/ZrO<sub>2</sub> G. Reaction conditions:  $T = 190^\circ \text{C}$ ,  $P_{\text{air}} = 50 \text{ bar}$ , liquid flow rate  $24 \text{ mL h}^{-1}$ , gas flow rate  $5 \text{ STP L h}^{-1}$ . There were some process upsets that occurred during the experiment (A: the air feed to the reactor was interrupted in two events lasting approximately 12 h, and B: electricity was cut a few hours).

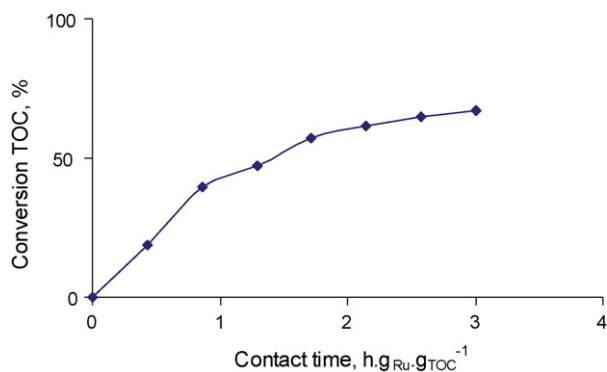


Fig. 10. TOC conversion as function of space time in the oxidation of 2% MIB in the presence of 3% Ru/TiO<sub>2</sub> G.

kept for anaerobic bio-treatment experiments. The other part was recycled six times to increase the contact time. The catalyst was relatively stable during the re-use experiments. The TOC conversion as a function of residence time is shown in Fig. 10. Conversion increased smoothly with residence time up to 67%. Analysis of the final effluent did not detect leached Ru or Ti.

These two continuous experiments performed on two different diluted Tunisian and Italian OMWs (TOC<sub>i</sub> = 930 and 8730 mg/L, respectively) show the potential of supported ruthenium catalysts for the elimination of TOC and phenolic compounds in OMW. The catalyst was stable, chemically and catalytically.

### 3.4. Effect of CWAQ pretreatment on anaerobic digestion

Because of the high organic load of OMW, purification by anaerobic digestion may constitute an appealing method from an energetic point of view to treat these wastes. But OMW contains various phenolic compounds that are inhibitors, decelerate the process and hinder removal of part of the COD [12]. Coupling chemical oxidation and anaerobic digestion has received much attention [26,29–32]. The goal is a mild oxidation in the first step of the toxic and inhibitory compounds like phenolic compounds into biodegradable intermediates, which can then be subsequently treated biologically.

Since the catalytic wet air oxidation of the OMWs reduced considerably the total phenolic compound concentration in diluted MTB, this effluent was also treated by a combined CWAQ–anaerobic process. The anaerobic digestion was carried out using (i) untreated diluted MTB and (ii) diluted MTB pretreated in the presence of catalyst 3% Ru/ZrO<sub>2</sub> G to eliminate 60% TOC (Fig. 6).

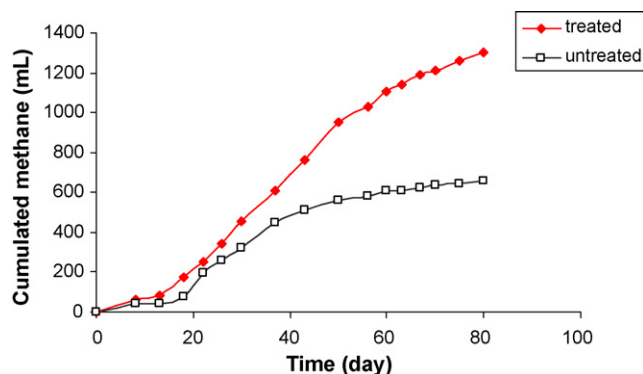


Fig. 11. Bioconversion (cumulated methane) versus time of untreated and treated diluted MTB in continuous anaerobic filters operated at 5 g COD per anaerobic batch culture.

Biotreatability tests were carried in 500 L anaerobic digesters fed discontinuously at a loading of 5 g COD per batch.

Fig. 11 shows the variation of the volume of methane accumulated as a function of time in the anaerobic digestion of the untreated OMW and pretreated OMW, respectively. These tests confirm the effectiveness of the pretreatment. Indeed, the methane production from untreated OMW showed a saturation profile, while the pretreated OMW maintained satisfactory methane production without remarkable inhibition effects. The biodegradability enhancement of the treated effluent may be attributed to the reduction of the total phenolic compounds concentration of the waste and of the associated toxicity, which facilitates the anaerobic digestion of the OMW.

## 4. Conclusion

The studies reported in this work indicate that catalytic wet air oxidation in the presence of Pt and Ru supported catalyst at the conditions employed may achieve high degree of mineralization of pollutants in OMW. Ru catalysts appear to be stable in the continuous experiments. The use of a heterogeneous catalyst also rapidly transformed the bioresistant phenolic compounds. As a consequence, the oxidized wastewater was made more amenable to further anaerobic digestion if compared to the non-treated wastewater. This resulted in an enhancement in the yield of methane production. A process combining catalytic oxidation for detoxification, followed by anaerobic digestion process may be thus suggested. Further studies and additional experimentations are required in order to choose the pretreatment operating conditions capable of optimizing the anaerobic digestion of OMW in both of kinetics and biomethane yield.

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